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Article

The Second Law Today: Using Maximum-Minimum Entropy Generation

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Abstract: There are a great number of thermodynamic schools, independent of each other, and without a powerful general approach, but with a split on non-equilibrium thermodynamics. In 1912, in relation to the stationary non-equilibrium states, Ehrenfest introduced the fundamental question on the existence of a functional that achieves its extreme value for stable states, as entropy does for the stationary states in equilibrium thermodynamics. Today, the new branch frontiers of science and engineering, from power engineering to environmental sciences, from chaos to complex systems, from life sciences to nanosciences, *etc.* require a unified approach in order to optimize results and obtain a powerful approach to non-equilibrium thermodynamics and open systems. In this paper, a generalization of the Gouy–Stodola approach is suggested as a possible answer to the Ehrenfest question.

Keywords: entropy; entropy generation; entropy production; irreversibility; second law analysis

PACS Codes: 05.70.-a; 05.70.Ln

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1. Introduction

During the XIXth century, thermodynamics began its development as a physical science as a result of the studies by Carnot (1796–1832), von Mayer (1814–1878), Helmholtz (1821–1894), Thomson (1824–1907) and Clausius (1822–1888) [1].

Clausius further developed the results of Helmholtz and Carnot, obtaining the first formulation of the second law as we know it nowadays. He suggested considering heat as a transformation of different kinds of energy, with the total energy remaining constant during the process. Indeed, he used Carnot's concept of the ideal cycle of a reversible heat engine in order to evaluate the work obtainable by transfer of heat from a high temperature to a lower temperature reservoir. Lastly, he introduced entropy and its mathematical expression. In 1851, Thomson independently obtained another formulation of the second law; he stated that it is impossible to create work by cooling down only one thermal reservoir. Therefore, the fundamentals of the second law result in a selection principle meaning an exclusion principle so that not all processes may be real, even if they are allowed by the energy conservation law [1]. Consequently, in order to study the evolution of the real processes, in the 1850s–60s, Clausius introduced a new quantity, *i.e.*, entropy [2].

In 1871, Boltzmann (1844–1906) introduced both the ergodic hypothesis, *i.e.*, all accessible microstates are equally probable over a long period of time, and, one year later, the H-theorem, the first link between the second law and the statistical approach to entropy. Then, in 1889, Planck (1858–1947) highlighted the fundamental role of entropy and its statistical interpretation. Later, Gibbs (1839–1903) developed the ensemble approach and the entropy functional. He highlighted the fundamental role of the maximum entropy approach in the analysis of natural systems: this principle has been improved by proving that the entropy variation due to irreversibility, during a process, is maximum if evaluated outside of the system and minimum if evaluated inside the system [3].

In 1909, Caratheodory (1873–1950) suggested an axiomatic formulation of thermodynamics based on the Pfaffian differential forms [4]. However, in 1929, Schottky (1886–1976) first extended the approach to thermodynamics for industrial applications. Recently, both thermodynamic formalism and the links between macroscopic and microscopic approaches to entropy, have been shown to play an important role in nonlinear sciences and complex systems, with particular regard to power engineering, environmental sciences, quantum theory, low temperature physics, large scale and small scale physics, biophysics, biochemistry and biomedicine, information sciences, *etc.* Nevertheless, Maxwell (1831–1879) was the first scientist interested in the relation between observer and object, information and entropy. Then Szilard (1898–1964), von Neumann (1903–1957), Birkhoff (1911–1996), Jaynes (1922–1998) and Friden developed this topic obtaining the link between the foundations of statistical physics with information theory, just by using the maximum entropy principle. It states that the probability distribution is such that uncertainty remains largest in relation to the constraints [3–10]. The analysis of the self-organization systems specifically refer to this topic. Introduced by Mayer, Boltzmann, Schrödinger (1887–1961) and Prigogine (1917–2003), it is based on the fundamental role of the fluxes between the system and its surroundings [3].

Related to this topic, the development of non-equilibrium or irreversible thermodynamics [6] must also be considered. This was begun by Thomson (1856–1940), Rayleigh (1842–1919), P Duhem (1861–1916), Natanson (1864–1937), and Jaumann (1863–1924) and formalized by Gouy (1854–1926),

Stodola (1859–1942), Onsager (1903–1976), Eckart (1902–1973), Meixner (1908–1994), Casimir (1909–2000), Prigogine and De Groot (1916–1994) [5–18]. Indeed, the analysis of irreversible processes is essential to study nonlinear sciences, which need a nonlinear dynamic approach. In this context, the evolutionary principles of the open systems and the related evolution of information-processing in Nature represent the present basic open problems in the thermodynamics field. In particular, the problem consists of the possibility of formulating a universal law of evolution for open systems. Moreover, in relation to the formulation of a unified approach useful for describing the evolution of open systems, why does a general agreement among scientists and engineers still not exist [19]?

For isolated systems (the ideal systems for real adiabatic closed systems), the second law of thermodynamics defines the state of maximum entropy as the equilibrium state. Therefore, when an isolated system is not in a state of maximum entropy, it spontaneously changes its entropy in order to achieve the nearest state of maximum entropy [19–24]. For example, Onsager proved that *linear* non-equilibrium thermodynamic analyses can be based on the principle of the least energy dissipation [5], which is equivalent to the maximum entropy production principle [3]. Again, for a rarefied gas in a state close to equilibrium, the solution of the linearized Boltzmann equation leads to maximum entropy production [19]. Moreover, we must foreground how the thermodynamicists usually use the terms "entropy generation" and "entropy production". However, nothing is really produced or generated; entropy varies in relation to energy and mass fluxes and to irreversibility, but it is not produced or generated. Many authors [24–37] have developed different approaches but criticisms [23,38,39] have been advanced for each of them.

The result is a great number of thermodynamic schools, without a powerful general approach, but with a split on non-equilibrium thermodynamics. In 1912, in relation to the stationary non-equilibrium states, Ehrenfest introduced the fundamental question on the existence of a functional, which achieves its extreme value, as entropy does for the stationary states in equilibrium thermodynamics. Today, the new branch frontiers of science and engineering, from power engineering to environmental sciences, from chaos to complex systems, from life sciences to nano-sciences, *etc.* require a unified approach in order to optimize results and obtain a powerful approach to non-equilibrium thermodynamics and open systems. In this paper, an approach based on the energy wasted in the environment is suggested.

2. The Analytical Formulations of Second Law

There are many analytical formulations of the second law: each of them represents a dissipation inequality. Meixner introduced two different temperatures, the equilibrium and the non-equilibrium temperature [40], while Gurtin and Williams introduced the surface and the bulk temperature [41]. In relation to the definition of temperature, we must first note the fact that the equilibrium temperature is defined in an operative way, and that, often, different definitions are only mathematical relations. More clarity appears to be fundamental for an exhaustive definition of temperature.

In order to introduce the hypothesis of equilibrium useful to define the thermodynamic quantities, the phase space of irreversible thermodynamics is an equilibrium subspace. On the other hand, in extended irreversible thermodynamics the choice of a new state space [42] does not require local equilibrium.

In rational, endoreversible and non-equilibrium thermodynamics, local equilibrium is introduced [42]. The concept of local equilibrium is useful in order to define the thermodynamic quantities T and entropy S, as is usually done in classical thermodynamics. Indeed, we follow this thermodynamic approach defining temperature and entropy in relation to local equilibrium as in Ref. [5].

In the years 1850–1865, Clausius introduced the notion of entropy S writing its elementary change as:

$$dS = \frac{\delta Q}{T} \tag{1}$$

where δQ is the heat exchanged by the system at absolute temperature T in a reversible process. The existence of a single-valued state function, entropy, represents the essence of the second law for macroscopic systems [38]. The most effective and accepted way to formulate the second law is the Clausius inequality for a closed system [5]:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{2}$$

which represents global dissipation inequality.

For an open system, analysis is more complex. Indeed, the entropy variation with time t inside the control volume is the result of the entropy variation inside system, dS_{in}/dt, and the entropy variation due to heat and mass flows $\mathbf{J}_s$ across boundary surface A [5]:

$$\frac{dS}{dt} = \frac{dS_{in}}{dt} - \int_A \mathbf{J}_s \cdot \mathbf{n} dA \tag{3}$$

being $\mathbf{n}$ the exit unitary vector perpendicular to elementary boundary surface dA, and dS_{in} the entropy increase due to internal irreversibilities. We define entropy generation as the entropy variation of the system considered, and entropy production as the entropy generation in the time considered and per unit of volume, that is the density rate of entropy generation.

This global expression in a local form is [5]:

$$\rho \frac{ds}{dt} = \sigma - \nabla \cdot \mathbf{J}_s \tag{4}$$

with $\sigma \geq 0$. Under the hypothesis of local equilibrium, it is possible to introduce an evolutionary criterion that involves entropy production density σ [28–35] so that:

$$\left.\begin{array}{l} \sigma = \dfrac{\delta^2 S_{in}}{dVdt} = \sum_i X_i J_i = \mathbf{X} \cdot \mathbf{J} \\ \mathbf{X} = -\mathbf{\Lambda J} \\ d\sigma = d\mathbf{X} \cdot \mathbf{J} + \mathbf{X} \cdot d\mathbf{J} \end{array}\right\} \Rightarrow \frac{d\sigma}{dt} \leq 0 \tag{5}$$

which represents the Lyapunov property of the entropy production density itself [28], and where $\mathbf{X}$ are thermodynamic forces depending on the phenomenon considered, and $\mathbf{J}$ is the thermodynamic flux density. However, using the Lagrange multipliers method, a different result was obtained [38,39]:

$$\frac{d\sigma}{dt} \geq 0 \tag{6}$$

Consequently, a question arises: is entropy production density maximum or minimum [3,43–55]? This is a very interesting research topic; moreover, from an engineering thermodynamic point of view, it requires a fundamental, general principle, based on a macroscopic quantity. Consequently, it is interesting to develop a global analysis of the irreversibility in open and complex systems.

The study on the variational principles for dissipative mechanical systems has been a longstanding question [56–59] since 1744, when Euler developed the analysis of the brachistochrone problem with friction. The difficulties can be summarized as follows:

- only some special systems and frictions can be completely analysed;
- the Lagrangian loses its uniqueness;
- the link between Lagrangian and Hamiltonian cannot easily highlighted;
- the action behaviour is not clear for non-dissipative systems.

3. The Approach Suggested

The variational method is very important in mathematical and theoretical physics because it allows us to describe natural systems by physical quantities, independently from the frame of reference used. Indeed, the Lagrangian formulation is useful in a variety of physical phenomena and a structural analogy between different physical phenomena has been pointed out. The most important result of the variational principle consists in obtaining both local and global theories. A Lagrangian approach to entropy generation allowed mathematical relations to be obtained. Entropy generation allows a global description of any irreversible process, and interest in its applications is growing. Moreover, it has also been related to the thermodynamic Lagrangian, becoming the quantity, which can link the global and local approaches to the analysis of any irreversible system [3].

Consider an open, continuum or discrete, N particles system. Every i-th element of this system is located by a position vector $\mathbf{x}_i$, it has a velocity $\dot{\mathbf{x}}_i$, a mass m_i and a momentum $\mathbf{p}_i = m_i\dot{\mathbf{x}}_i$, with $i \in [1,N]$. The total mass of the system is $m = \sum_i m_i$ and its density is ρ. The position of the centre of mass is $\mathbf{x}_B$ and its velocity is defined as $\dot{\mathbf{x}}_B = \sum_i m_i \dot{\mathbf{x}}_i/m$, while the mean motion velocity, called diffusion velocity, is defined by the relation $\mathbf{u}_i = \dot{\mathbf{x}}_i - \dot{\mathbf{x}}_B$. The total mass of the system must be a conserved quantity, so it must satisfy the following relation $\dot{\rho} + \rho\nabla \cdot \dot{\mathbf{x}}_B = 0$ [40]. This global analytical relation must also be verified locally, related to the density of the i-th elementary volume of density ρ_i and a source Ξ generated by matter transfer, chemical reactions or thermodynamic transformations, as follows $\dot{\rho}_i + \rho_i\nabla \cdot \dot{\mathbf{x}}_i = \rho\Xi_i$ [40]. For an open system, as just described in a macroscopic way, the equation of the entropy balance Equation (4) can become [17]:

$$\frac{\partial s}{\partial t} + v\nabla \cdot \mathbf{J}_S = v\sigma \tag{7}$$

$$\mathbf{J}_S = \frac{\mathbf{Q}}{T} + \sum_i \rho_i s_i \mathbf{u}_i \tag{8}$$

where $s = S/V$, with S entropy, is the entropy density, v is the specific volume, σ is the entropy production and $\mathbf{J}_s$ is the entropy flux defined as in [40]: where $\mathbf{Q}$ is the heat flow vector. When a system with a temperature T receives reversibly a small amount of heat δQ, the entropy of the system will increase by an amount [5]:

$$S = \int_{is}^{fs} \frac{\delta Q}{T} \tag{9}$$

where S is the entropy variation of the system from the initial (*is*) and the final (*fs*) state of the process, δ represents an infinitesimal (or rather *elementary*) small change of a path function. The second law, as the law of entropy increases, is always valid for a completely isolated system, so it also remains valid for open systems, if the system and its surroundings/environment are considered as a whole system. When we sum up all the changes of entropy of interacting subsystems, the total change must be non- negative. Moreover, the maximum work is not attainable for natural systems where irreversible processes are inevitable. There is a natural tendency of various kinds of irreversible processes to dissipate mechanical into heat energy.

These considerations must be taken into account in the formulation of a general model of analysis of the thermodynamic processes introducing a quantity useful to describe the systems' evolution. Moreover, this physical quantity must be useful both in linear and in non-linear phenomena. So, in order to develop our approach, we introduce specific hypotheses [44,48]:

(1) an open irreversible real system with non-linear response is considered;
(2) each process has a finite lifetime τ [58]
(3) what happens in each instant in the range $[0,\tau]$ may not be known, but what has happened after the time τ (the result of the process) can be well known [12];
(4) for open system the entropy balance equation is a balance of fluxes of entropy;
(5) the Gouy–Stodola theorem works for real systems.

The usual thermodynamic balance is based on the variation of the entropy and three components for the entropy are considered: one related to external mass exchanges, one to heat exchanges $\delta S = \delta Q/T$, and the last related to the internal origin $\delta_{in}S = -X d\alpha$, with X non-conservative forces and α extensive thermodynamic quantities. The entropy S of the whole system (the control volume and the surroundings/environment) is a state function depending only on the equilibrium state of the system considered and only entropy differences can be evaluated in the lifetime of process τ and the equation of entropy balance for the system using Equation (7) results in:

$$\Delta S = \int_0^{\tau} dt \int_0^{V} v dv \left(\sigma - \nabla \cdot \mathbf{J}_S\right) = \Delta S_e + S_g \tag{10}$$

where $\mathbf{J}_S$ is the entropy flux Equation (8). The quantity ΔS_e should be better defined as the entropy variation due to the above mentioned fluxes throughout the system boundaries.

Entropy generation is then evaluable by the Gouy–Stodola theorem:

$$S_g = \frac{W_\lambda}{T_0} \tag{11}$$

with T_0 temperature of the surroundings/environment, W_λ dissipated work by irreversibility in the process lifetime τ considering Equation (10).

The relation between entropy production (rate) and entropy generation is:

$$S_g = \int_0^{\tau} dt \int_V v dV \sigma \tag{12}$$

In a variational approach to thermodynamics, the systems goes from the initial to the final state of the process with the lifetime τ, following a path that is the most probable path. Now, we must foreground the fact that in irreversible thermodynamics, the local Gyarmati principle is of universal validity and represents a fundamental reference for our improvements. Then, following Gyarmati [60], the thermodynamic Lagrangian density, ρ_L, is:

$$\rho_{\mathcal{L}} = T\sigma_v - \varphi \tag{13}$$

where ϕ is the dissipation functions so that [3]:

$$W_\lambda = \int_V \varphi dV \tag{14}$$

From Equation (5) the production density is:

$$\sigma_v = \frac{d}{dV}\int_0^{\tau} \sigma dt = \sum_i J_i X_i = \mathbf{J}\cdot\mathbf{X} \tag{15}$$

where τ is the lifetime of the process. Consequently, using Equations (11), (12) and (15), the thermodynamic Lagrangian becomes:

$$L = \int_V \rho_{\mathcal{L}} dV = \int_V \left(T\sigma_v - \varphi\right) dV = \int_V T\mathbf{J}\cdot\mathbf{X} dV - W_\lambda = T\int_V \mathbf{J}\cdot\mathbf{X} dV - T_0 S_g \tag{16}$$

Now, considering that $T\int_V \mathrm{J}\cdot\mathrm{X} dV = T\int_V dV \int_0^{\tau} dt\sigma = TS_g$ it follows that:

$$\mathcal{L} = TS_g - T_0 S_g = \left(T - T_0\right) S_g \tag{17}$$

Then, considering the definition of action:

$$\mathcal{A} = \int_0^{\tau} dt\mathcal{L} = \int_0^{\tau} \left(T\Delta S_i - T_0 S_g\right) dt = \int_0^{\tau} \left(T - T_0\right) S_g dt \tag{18}$$

applying the principle of least action δA = 0, it follows that the condition of evolution is [59]:

$$S_g dT + \left(T - T_0\right) dS_g \le 0 \Rightarrow S_g \le \frac{C}{T - T_0} \tag{19}$$

with *C* constant. This relation proves the existence of maximum in entropy production in the thermodynamic universe.

4. Fourier Law: An Example of Application of the Entropy Approach

The equation of heat conduction in solids is a fundamental subject of investigation in modern mathematical physics. Indeed, the approach used to obtain this equation was the basis of the mathematical formulation of many other physical processes related to diffusion. This topic could represent a very interesting application of previous results.

Fourier (1768–1830) first formulated the transient process of heat conduction. He obtained the partial differential equation by linking a rigorous mathematical approach to empirical observations [61]. Indeed, he submitted to the Institut de France in December 1807, his memoir on "*Théorie de la Propagation de la Chaleur dans les Solides*", which was never accepted. His theory was completely explained in the monograph "*Théorie analytique de la chaleur*" [62].

Fourier's equation describes the macroscopic transport of heat in non-equilibrium systems, so his approach can be used to describe all the transport phenomena.

Let us consider a rigid solid body of a homogeneous material with mass density ρ. On the border surfaces, there is a temperature gradient. Inside this body, we analyze a small volume. For this system, the second law holds:

$$\frac{\partial}{\partial \tau}\left[\int_V \rho s dV\right] = \int_A \frac{1}{T}\mathbf{q}\mathbf{n}dA + \frac{\partial}{\partial \tau}\left[\int_V \rho s_g dV\right] = \int_V \nabla\frac{1}{T}\mathbf{q}dV + \frac{\partial}{\partial \tau}\left[\int_V \rho s_g dV\right] \tag{20}$$

With **q** the unitary heat flux. Applying the previous results to an infinitesimal volume *dV*, it follows that the first derivative of the entropy generation results as:

$$\rho\frac{ds_g}{d\tau}dV = \rho\dot{s}\ dV + \mathbf{q}(\mathbf{r})\cdot\mathbf{r}dA(r)\frac{1}{T^2}\nabla T\cdot\frac{\mathbf{r}}{r} + \frac{1}{T}(\nabla\mathbf{q}\cdot d\mathbf{r})\cdot\mathbf{r}dA(r) \tag{21}$$

where $A(r)$ is the area of the section perpendicular to direction **r** considered and:

$$\mathbf{q}(\mathbf{r}+d\mathbf{r}) = \mathbf{q}(\mathbf{r}) + \nabla\mathbf{q}\cdot d\mathbf{r} \tag{22}$$

Considering the first law:

$$du = \delta q - \delta l \tag{23}$$

with $\delta l = 0$ and $du = cdT$ for a solid body. From the energy balance, it follows that:

$$\dot{q} = \rho c\frac{dT}{d\tau} = \rho\frac{du}{d\tau} \tag{24}$$

using the entropy definition:

$$\rho\dot{s}_g dV = \frac{\rho}{T}\frac{du}{d\tau}dV + \mathbf{q}(\mathbf{r})\cdot\mathbf{r}\frac{\nabla T}{T^2}\cdot\frac{\mathbf{r}}{r}dA - \rho\frac{du}{d\tau}\frac{dV}{T} = \left[\mathbf{q}(\mathbf{r})\cdot\mathbf{r}\right]\left[\frac{\nabla T}{T^2}\cdot\frac{\mathbf{r}}{r}\right]dA(r) \tag{25}$$

and considering that $\mathbf{r}dA = (\mathbf{r}/r)dV$ and Equation (12), it follows that:

$$\rho\dot{s}_g = \sigma = \left[\mathbf{q}(\mathbf{r})\cdot\frac{\mathbf{r}}{r}\right]\left[\frac{\nabla T}{T^2}\cdot\frac{\mathbf{r}}{r}\right]\frac{rdA(r)}{dV} \tag{26}$$

i.e., the entropy production per unit volume, which is constant for stationary conditions. Then:

$$\frac{d\sigma}{d\tau} = 0 \Rightarrow \frac{d(\nabla T)}{d\tau} = 0 \Rightarrow \nabla T = -\frac{1}{k}\mathbf{q} \tag{27}$$

which is precisely Fourier's law. Now, using the geometric frame so that the **r** axis is parallel to the temperature gradient the relation Equation (26) can be written as:

$$\rho\dot{s}_g = \sigma = \mathbf{q}(\mathbf{r})\cdot\frac{\nabla T}{T^2} = -\mathbf{q}(\mathbf{r})\cdot\nabla\left(\frac{1}{T}\right) \tag{28}$$

Now, considering the relations Equations (19), (27) and (28) it follows that:

$$-k\left(\frac{\nabla T}{T}\right)^2 V\tau \le \frac{C}{T-T_0} \tag{29}$$

always verified. Consequently, Fourier's law results from the second law in stationary conditions and in agreement with the Gouy–Stodola theorem. The natural behaviour of the conduction is to transfer heat on the path of maximum entropy generation. A numerical application as a particular case can be found in [63].

5. Conclusions

There are a great number of variational approaches to thermodynamics, but none of them can present a unified model in applied thermodynamics, because the thermodynamicists do not unanimously accept it.

Applied thermodynamics is the science that studies both energy and its best use in relation to available energy resources. Considering energy as the possibility to exchange work, it is usual to define an internal energy, which characterizes any state of a system in relation to a reference state, and exchanged energy as work or heat. During any interaction, the total amount of energy is always constant in the universe (the system and its environment). So, its physical meaning is related to its exchange. Indeed, useful work is obtained by evaluating the variations of the energy of the system, which means that any change in a system always relates to a transition between different system states.

Carnot's results on heat engines imply the existence of a well calculable limit for any conversion rate of heat into kinetic energy and work. Clausius, in order to analyse dissipative processes, introduced entropy. In 1889, Gouy [64] and Stodola in 1905 [65], independently proved that the lost exergy in a process is proportional to entropy generation. Consequently, it is interesting to introduce a principle of evolution of the systems, based on the analysis of the interaction between systems and their environment.

This approach can be based precisely on the Gouy–Stodola theorem, because it allows us to evaluate the irreversibility and dissipations in the interaction between systems and their environment, by considering entropy generation, which is related to the energy the systems lose during any interaction.

Using the above procedure, we have shown how Fourier's law for conduction in solids can be derived from the second law under stationary conditions.

Author Contributions

Umberto Lucia and Giuseppe Grazzini contributed equally to the paper. Umberto Lucia and Giuseppe Grazzini wrote the paper together.

Conflicts of Interest

The authors declare no conflict of interest.

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